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## (54) Easily sievable powder coating composition

(57) Finely divided hydrophobic silica powder having a number average particle size from 3 to 10 nm and a BET surface area from 195 to 290 m<sup>2</sup>/g is dry blended with particles of a thermosetting resin composition having a volumetric average particle size from 5 to 20 µm in a proportion from 0.05 to 2.0 parts per 100 parts of the resin particles on weight basis. The sieving efficiency of the powder coating composition thus processed is improved.

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## EASILY SIEVABLE POWDER COATING COMPOSITION

This invention relates to a powder coating composition  
5 which is easy to handle, particularly to sieve.

Powder coating technology has become popular in  
finishing automobile bodies and parts, household electrical  
appliances and building materials because it does not use  
any organic solvents which present environmental pollution  
10 problems.

Powder coating compositions are generally produced by  
blending a binder resin with a curing agent and optionally  
other additives such as pigments, kneading the mixture under  
heat to make a molten mass, pulverizing the solidified  
15 mass and then classifying the pulverized powder. The powder  
thus produced is applied onto a substrate using the  
electrostatic spray coating method or fluidized bed coating  
method to form a film, and then baked to form a cured film.  
The powder is sieved on site immediately before use to  
20 remove any agglomerated particles formed by blocking during  
transporting and storage. Portions of the powder not  
deposited onto the substrate are recovered and sieved to  
remove agglomerated particles and any particulate foreign  
matter to recycle the recovered powder.

25 Solvent type coating compositions have been

conventionally used in fields in which a highly aesthetic finish is critical. In order to use the powder coating composition in such fields, the powder must have a volumetric average particle size as fine as from 5 to 20  $\mu$  m. However, powder with a particle size in this range cannot be efficiently sieved, not only in the classifying step of the powder as produced but also in the sieving step on site before or after the application onto the substrate, because the powder tends to clog sieving screens more frequently than powder with larger particle sizes.

Therefore, a need exists for a powder coating composition which does not present the above problem in sieving.

The present invention provides a powder coating composition comprising particles of a thermosetting resin composition having a volumetric average particle size from 5 to 20  $\mu$  m, and from 0.05 to 2.0 parts by weight per 100 parts by weight of said particles of finely divided hydrophobic silica powder having a number average particle size from 3 to 10 nm and a BET surface area from 195 to 290 L/g, said silica powder being dry blended with said particles.

In a preferred embodiment, said finely divided silica powder has a BET surface area from 230 to 290 L/g and has

been surface-treated to block silanol groups on the surfaces thereof with a hydrophobic blocking agent.

The powder coating composition of the present invention  
5 comprises particles of a thermosetting resin composition and finely divided hydrophobic silica powder dry blended with the resin particles. The term "particles of a thermosetting resin composition" as used herein refers to particles containing a binder resin, a curing agent and  
10 other additives produced by, as stated above, pulverizing a molten and then solidified mixture of the above components.

Except for the presence of fine silica powder, the inventive powder coating composition is otherwise identical to conventional powder coating compositions. Because of  
15 this, any component including the binder resin, curing agent and other additives known in the art may be used for producing the thermosetting resin particles.

The binder resin must be a solid at room temperature and has a melting point from 120°C to 200 °C . The resin must  
20 also be capable of curing with an external curing agent. Typical examples thereof are polyester, epoxy or acrylic resins. When a high weatherability is desired, acrylic binder resins are used. Polyester resins are polycondensates of a polyhydric alcohol component such as ethylene glycol,  
25 propanediol, pentanediol, hexanediol, neopentyl glycol,

trimethylolpropane or pentaerythritol, and a polycarboxylic acid component such as tetraphthalic, isophthalic, phthalic, succinic, glutaric, adipic, sebacic or  $\beta$ -hydroxypropionic acid. Any type of epoxy resins may be used provided they have a plurality of oxirane rings in the molecules. Typical examples are glycidyl ester type epoxy resins, glycidyl ether type epoxy resins represented by bisphenol A epoxy resins, alicyclic epoxy resins, and linear aliphatic epoxy resins. Acrylic binder resins are produced by copolymerizing an ethylenically unsaturated monomer such as styrene, methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate or t-butyl (meth)acrylate with a functional acrylic monomer such as (meth)acrylic acid, glycidyl (meth)acrylate, or 2-methylglycidyl (meth)acrylate. The binder resin preferably has a Tg of at least 30°C for preventing thermal deposition of resin particles to mill walls during the pulverizing step. The Tg of the binder resin preferably does not exceed 55 °C so that a flat film surface is formed by baking.

Curing agents are selected depending upon the type of functional group possessed by the binder resin. For polyester resins, polycarboxylic acids, melamine resins or blocked polyisocyanates are used. For epoxy resins, polycarboxylic acid anhydrides, dicyandimide or acrylic resins are used. For acrylic resins, polycarboxylic acid

anhydrides, epoxy resins or aminoplast resins are used.

Examples of pigments are coloring pigments such as titanium dioxide, iron oxide, carbon black, phthalocyanine blue, phthalocyanine green, quinacridone pigments or azo pigments, and extender pigments such as talc, calcium carbonate or precipitated barium sulfate. Examples of other additives are surface conditioners such as polysiloxane or acrylic resin, plasticizers, UV absorbers, antioxidants, anti-cratering agents, pigment dispersants, curing catalysts and benzoin compounds.

The above materials are premixed in a mixer such as a super mixer or Henschel mixer before kneading under heat, wherein various materials are dispersed in molten state at molecular levels. Busco kneaders or extruders are used in the kneading step. Then the resulting hot mass is rolled into a sheet and allowed to solidify by cooling, followed by crushing into chips and pulverizing into fine particles having a desired particle size. Typically, super mixers, Henschel mixers or jet mills are used for producing fine particles. Before packaging, the fine particles are classified into a desired particle size distribution suitable for the intended application. During the classifying step, coarse particles or finer particles or both are removed.

Thermosetting resin particles thus produced are

packaged in a container and then shipped. In use, they are sieved before filling into a powder holder of an applicator machine to remove large agglomerated particles formed by the blocking of individual particles during transportation  
5 and storage periods. In the electrostatic spray method, particles not deposited onto the substrate are recovered and reused after blending with fresh particles. Since recovered particles contain dust and other particulate foreign matter, this particulate foreign matter must be  
10 removed by sieving.

Resin particles as fine as 20  $\mu$ m or less in volumetric average particle size for use in highly aesthetic finishes have a remarkable tendency to clog wire screens of 42 to 325 mesh, even when sieved under vibration.  
15 Dry blending of finely divided hydrophobic silica powder as defined herein facilitates not only classifying the resin particles as produced, but also the sieving thereof on site.

According to the present invention, the finely divided hydrophobic silica powder must have a number average particle size from 3 to 10 nm and a BET surface area from 195 to 290 L/g, preferably from 230 to 290 L/g. Preferably, the silica powder is surface-treated to block silanol groups on the surfaces thereof with a hydrophobic blocking agent or a hydrophobic silane coupling agent such as  
25 monoalkyltrihalosilane, dialkyldihalosilane or

trialkylmonochalosilane. Hydrophobic silica powder meeting the above parameters is commercially available. Examples thereof include AEROSIL R-812 and AEROSIL R-812S both sold by Nippon Aerosil K.K. AEROSIL R-812S is particularly preferred. Other commercial products comparable to the above products may also be used.

The amount of the silica powder generally ranges between 0.05 to 2.0 parts, preferably between 0.1 and 1.0 parts by weight per 100 parts by weight of the resin particles not containing the silica powder. Excessive addition of the silica powder will adversely affect the flatness or other appearance properties of cured films.

Dry blending of the silica powder may be conducted before, during or after the classifying step of resin particles, provided that the silica powder particles are not embedded in the resin particles.

The powder coating composition of the present invention is well suited to the electrostatic spray coating method including the corona charging and frictional charging spray coating methods.

The following examples are given for illustrative purposes only but are not limiting. All parts and percents therein are by weight unless otherwise specified.

**Production Example 1**

25      Acrylic Binder Resin

A reaction vessel equipped with a thermometer, stirrer, condenser, nitrogen gas tube and drip funnel was charged with 63 parts of xylene and then heated to 130°C. To this were added dropwise a monomer mixture consisting of 45 parts of glycidyl methacrylate, 20 parts of styrene, 27 parts of methyl methacrylate and 8 parts of isobutyl methacrylate, and a solution of 6.5 parts of t-butylperoxy 2-ethylhexanoate in 6 parts of xylene over 3 hours using the drip funnel. After the addition, the reaction mixture was kept at 130 °C for 30 minutes. Then a solution of 6.1 parts of t-butylperoxy 2-ethylhexanoate in 7 parts of xylene was added dropwise and the reaction mixture maintained at 130°C for 1 hour. After removing the xylene by distillation in vacuo, an acrylic resin having a Tg of 55°C and a number average molecular weight of 3,200 measured by the GPC method using polystyrene standard was obtained.

Example 1

Acrylic Powder Coating Composition

	<u>Material</u>	<u>Parts</u>
20	Acrylic resin of Production Example 1	48
	Decanedicarboxylic acid	12
	Surface conditioner (CF-1056 sold by Toshiba silicone K.K.)	0.1
	Benzoin	0.3
25	Bisphenol A epoxy resin, YD-012 sold by Toto Kasei K.K.	2.2

The above materials were premixed in a super mixer  
(Nippon Spindle K.K.) for 3 minutes. The premix was  
transferred to a kneader sold by Busco and kneaded at 100 °C  
5 . The resulting hot mass was cooled to room temperature,  
crushed, pulverized in an atomizer sold by Fuji Powdal K.K.  
and classified pneumatically using a pneumatic classifier  
Model DS-2 sold by Nippon Pneumatic Industry K.K.  
Thermosetting resin particles having a volumetric average  
10 particle size of 10  $\mu\text{m}$  were obtained.

100 parts of resin particles thus produced were placed  
in a Henschel mixer and mixed with 0.5 parts of AEROSIL R-  
812S (Nippon Aerosil K.K., nominal number average particle  
size of 7 nm, nominal BET surface area of 260 L/g) for 1  
15 minute.

#### Examples 2 and 3

Example 1 was followed except that the amount of  
AEROSIL R-812S was changed to 0.25 parts and 1.0 part,  
respectively.

#### 20 Example 4

Example 1 was followed except that AEROSIL R-812S was  
replaced with 0.5 parts of AEROSIL R-812 (Nippon Aerosil  
K.K., nominal number average particle size of 7 nm, nominal  
BET surface area of 220 L/g).

#### 25 Comparative Example 1

Example 1 was followed except that AEROSIL R-812S was replaced with 0.5 parts of AEROSIL 300 (hydrophilic silica powder having a nominal particle size of 7 nm and a nominal BET surface area of 300 L/g, Nippon Aerosil K.K.).

5 Comparative Example 2

Example 1 was followed except that AEROSIL R-812S was not added.

Comparative Example 3

Example 1 was followed except that the amount of  
10 AEROSIL R-812S was increased to 3.0 parts.

Comparative Example 4

Example 1 was followed except that AEROSIL R-812S was changed to 0.5 parts of AEROSIL R-974 (hydrophobic silica powder having a nominal particle size of 16 nm and a  
15 nominal BET surface area of 110 L/g).

Example 5

Polyester Powder Coating Composition

<u>Material</u>	<u>Parts</u>
Polyester resin (FINEDIC M8021, Dainippon Ink And Chemicals Inc.)	60
20 $\epsilon$ -Caprolactam blocked polyisocyanate (ADDUCT B-1530, Huels)	10
Calcium carbonate	5
Titanium dioxide	20
Surface conditioner (F-1056)	0.5

The above materials were processed as in Example 1 to obtain thermosetting resin particles having a volumetric average particle size of 10  $\mu$ m. 100 parts of the resulting resin particles were processed with 0.5 parts 5 of AEROSIL R-812S as in Example 1.

**Comparative Example 5**

Example 5 was followed except that AEROSIL R-812S was not added.

**Example 6**

10 **Epoxy Powder Coating Composition**

Material	Parts
Epoxy resin (EPIKOTE 1002, Yuka Shell Epoxy K.K.)	65
Dicyandiamide	5
Titanium dioxide	20
15 Calcium carbonate	5
Surface conditioner (F-1056)	0.5

The above materials were processed as in Example 1 to obtain thermosetting resin particles having a 20 volumetric average particle size of 10  $\mu$ m. 100 parts of the resulting resin particles were processed with 0.5 parts of AEROSIL R-812S as in Example 1.

**Comparative Example 6**

Example 6 was followed except that AEROSIL R-812S was 25 not added.

Evaluation

Powder compositions of Examples 1-6 and Comparative Examples 1-6 were tested for angle of repose, sievability and film appearance according to the following methods. The results obtained are shown in Table 1 and Table 2 below.

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Tg:

Measurement was made using a differential scanning calorimeter sold by Seiko Instruments Inc., under the name of SEIKO I SSC/5200.

10

Angle of repose:

The measurement was made using a powder tester sold by Hosokawa Micron K.K. under the name of Powder Tester PT-D.

Sievability:

Measurement was made using the above Powder Tester PT-D. A plastic bag is attached to the bottom of a circular 60 mesh sieve having a diameter of 20 cm. The sieve is attached to the tester and vibrated vertically at an amplitude of 1 mm. 100 g of sample is added rapidly to the sieve and time counting is started. After the vibration for 20 seconds, sieving is stopped and the weight of sample passed through the sieve during this period is measured. The measured weight is converted to a value representing the weight of sample passed during the period of 1 minute.

Film appearance:

25

Each coating composition was applied by the

electrostatic spray method onto a zinc phosphate treated  
steel plate to a film thickness of  $60 \pm 5 \mu\text{m}$ , and then  
baked at  $140^\circ\text{C}$  for 20 minutes in a hot air oven. The film  
appearance was evaluated in terms of NSIC (%) measured by a  
5 reflected image distinctiveness meter sold by Suga Testing  
Instrument Co., Ltd.

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table 1

<u>Item</u>	<u>Example</u>					
	1	2	3	4	5	6
<u>Resin particle</u>						
<u>Resin type</u>	Acrylic	Acrylic	Acrylic	Acrylic	Polyester	Epoxy
<u>Particle size, <math>\mu</math> m</u>	10	10	10	10	10	10
<u>Parts</u>	100	100	100	100	100	100
<u>Fine silica powder</u>	R-812S	R-812S	R-812S	R-812	R-812S	R-812S
<u>AEROSIL</u>						
<u>Particle size, nm</u>	7	7	7	7	7	7
<u>BET surface area, L/g</u>	260	260	260	220	260	260
<u>Parts</u>	0.5	0.25	1.0	0.5	0.5	0.5
<u>Angle of repose, degree</u>	43	44	42	43	42	42
<u>Weight passed, g/minute</u>	376	361	383	328	380	385
<u>NSIC, %</u>	65	71	63	64	40	39

Table 2

Item	Comparative Example					
	1	2	3	4	5	6
Resin particle						
Resin type	Acrylic	Acrylic	Acrylic	Acrylic	Polyester	Epoxy
Particle size, $\mu$ m	10	10	10	10	10	10
Parts	100	100	100	100	100	100
Fine silica powder						
AEROSIL	300	Not added	R-812S	R-974	Not added	Not added
Particle size, nm	7	7	7	16		
BET surface area, L/g	300	260	260	110		
Parts	0.5	3.0	0.5			
Angle of repose, degree	49	50	42	44	49	48
Weight passed, g/minute	82	74	403	244	94	98
NSIC, %	54	75	55	65	41	42

From the results shown in Table 1 and Table 2, it is clear that the sievability of the powder coating compositions of Examples 1-6 increase at least 4 times compared with corresponding compositions of Comparative Examples 2,5 and

5 6 not containing the hydrophobic fine silica powder.

Comparative Example 3 demonstrates that excessive addition of the silica powder adversely affects the film appearance.

Comparative Examples 1 and 4 demonstrate that the addition 10 of fine silica powder having a hydrophilic nature or larger particle sizes are not effective to improve the sievability as desired.

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○ CLAIMS:

1. A powder coating composition comprising particles of a thermosetting resin composition having a volumetric average particle size from 5 to 20  $\mu\text{m}$ , and from 0.05 to 2.0 parts by weight per 100 parts by weight of said resin particles of finely divided hydrophobic silica powder having a number average particle size from 3 to 10 nm and a BET surface area from 195 to 290 L/g.
- 10 2. A powder coating composition as claimed in claim 1 wherein said silica powder is dry blended with said resin particles.
- 15 3. A powder coating composition as claimed in claim 1 or claim 2 wherein said silica powder has been surface-treated with a silane coupling agent to block at least a portion of the silanol groups present on the surfaces of said silica powder with a hydrophobic group.
- 20 4. A powder coating composition as claimed in any one of the preceding claims wherein said BET surface area is from 230 to 290 L/g.
- 25 5. A powder coating composition as claimed in any one of the preceding claims wherein said thermosetting resin comprises an acrylic, polyester or epoxy binder resin and a curing agent thereof.
6. A powder coating composition as claimed in claim 5 wherein said acrylic binder resin has a Tg from 30 to 55°C and a number average molecular weight from 1,000 to 4,000.

7. A method for improving the sievability of  
particles of a thermosetting resin composition used in  
powder coating technology, wherein from 0.05 to 2.0  
parts by weight of finely divided hydrophobic silica  
5 powder having a number average particle size from 3 to  
10 nm and a BET surface area from 195 to 290 L/g are dry  
blended per 100 parts by weight of said thermosetting  
resin particles having a volumetric average particle  
size from 5 to 20  $\mu\text{m}$ .

10 8. A method as claimed in claim 7 wherein said  
silica powder is surface-treated with a silane coupling  
agent to block at least a portion of the silanol groups  
present on the surfaces with a hydrophobic group.

9. A process for preparing a powder coating  
15 composition comprising particles of a thermosetting  
resin composition, said process comprising dry blending  
100 parts by weight of a thermosetting resin composition  
having a volumetric average particle size from 5 to  
20  $\mu\text{m}$ ; and 0.5 to 2.0 parts by weight of finely divided  
20 hydrophobic silica powder having a number average  
particle size of 3 to 10 nm and a BET surface area from  
195 to 290 L/g.

10. A process for preparing a powder coating  
composition as claimed in claim 9 wherein said silica  
25 powder is surface-treated with a silane coupling agent  
to block at least a portion of the silanol groups  
present on the surfaces of said silica powder with a  
hydrophobic group.

11. A powder coating composition prepared by a process as claimed in claim 9 or claim 10.

12. A powder coating composition substantially as herein described with reference to the Examples.



The  
**Patent  
Office**

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Application No: GB 9706211.1

Examiner: Miss Maureen M.  
Kelman

Claims searched: 1 to 12

Date of search: 25 June 1997

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3K KJA KXX, C3V VCA

Int Cl (Ed.6): C09D 5/00, 5/03, 5/46, 7/00, 7/06, 7/12, 133/00, 133/02, 133/14,  
163/02, 163/04, 167/02, 167/03

Other: ONLINE: CHABS, CLAIMS, JAPIO, RAPRA, WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0493076 A2 SOMAR see the claims and Example 1	1 to 5, 7 to 12
X	EP 0300818 A2 ICI AUSTRALIA see Examples 1 and 3	1,2,4,5,7, 9,11,12
X	WO 94/11446 A1 COURTAULDS COATINGS see claims 1,4,5,8,9,10,11,15 and 22, page 9, lines 10 to 11, Table 6 on page 48 and Table 9 on page 53	1,2,4,5,7, 9,11,12
X	US 5206332 A SKW TROSTBERG see claims 1,4,5,13,16 and 17 and the Examples	1 to 5, 7 to 12
X	US 5049596 A SOMAR see claims 1 and 2, column 3, line 59, to column 4, line 1, and Table 1	1 to 5, 7 to 12
X,P	JAPIO Abstract No: 05328117 & JP080283617 A (TOMOEGAWA PAPER) 29 October 1996 see abstract	1 to 5, 7 to 12
X,P	WPI Abstract Accession No: 96-408590 & JP080199090 A (NIPPON CARBIDE) 06 August 1996 see abstract	1,2,5,7,9, 11,12

- X Document indicating lack of novelty or inventive step  
Y Document indicating lack of inventive step if combined with one or more other documents of same category.  
& Member of the same patent family

- A Document indicating technological background and/or state of the art.  
P Document published on or after the declared priority date but before the filing date of this invention.  
E Patent document published on or after, but with priority date earlier than, the filing date of this application.



The  
Patent  
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**Claims searched:** 1 to 12

**Date of search:** 25 June 1997

Category	Identity of document and relevant passage	Relevant to claims
X	WPI Abstract Accession No: 86-336203 & JP061252276 A (TOMOEGAWA PAPER) 10 November 1986 see abstract	1 to 5, 7 to 12

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|---|--|
| <input checked="" type="checkbox"/> X Document indicating lack of novelty or inventive step   | A Document indicating technological background and/or state of the art.  |
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